

Environmental Barrier Coatings for Silicon-Based Ceramics

K. N. Lee, D. S. Fox, R. C. Robinson, and N. P. Bansal
NASA Glenn Research Center, Cleveland, OH 44135, USA

1 Introduction

Silicon-based ceramics, such as SiC fiber-reinforced SiC (SiC/SiC) ceramic matrix composites (CMC) and monolithic silicon nitride (Si₃N₄), are prime candidates for hot section structural components of next generation gas turbine engines. Silicon-based ceramics, however, suffer from rapid surface recession in combustion environments due to volatilization of the silica scale via reaction with water vapor, a major product of combustion (1, 2). Therefore, application of silicon-based ceramic components in the hot section of advanced gas turbine engines requires development of a reliable method to protect the ceramic from environmental attack. An external environmental barrier coating (EBC) is considered a logical approach to achieve protection and long-term stability (3).

The first generation EBC consisted of two layers, mullite (3Al₂O₃-2SiO₂) bond coat and yttria-stabilized zirconia (YSZ, ZrO₂-8 wt.% Y₂O₃) top coat (4). Second generation EBCs, with substantially improved performance compared with the first generation EBC, were developed in the NASA High Speed Research-Enabling Propulsion Materials (HSR-EPM) Program (5). They consist of three layers, a silicon first bond coat, a mullite or a mullite + BSAS (BaO_{1-x}-SrO_x-Al₂O₃-2SiO₂) second bond coat, and a BSAS top coat. The EPM EBCs were applied on SiC/SiC CMC combustor liners in three Solar Turbines (San Diego, CA) Centaur 50s gas turbine engines. The combined operation of the three engines has accumulated over 24,000 hours without failure (~1,250°C maximum combustor liner temperature), with the engine in Texaco, Bakersfield, CA, accumulating about 14,000 hours (6).

As the commercialization of Si-based ceramic components in gas turbines is on the horizon, a major emphasis is placed on EBCs for two reasons. First, they are absolute necessity for the protection of Si-based ceramics from water vapor. Second, they can enable a major enhancement in the performance of gas turbines by creating temperature gradients with the incorporation of a low thermal conductivity layer. Thorough understanding of current state-of-the-art EBCs will provide the foundation upon which development of future EBCs will be based. Phase stability and thermal conductivity of EPM EBCs are published elsewhere (7, 8) This paper will discuss the chemical/environmental durability and silica volatility of EPM EBCs and their impact on the coating's upper temperature limit.

2 Experimental

EBCs were applied at NASA Glenn Research Center by atmospheric pressure plasma spraying onto sintered α-SiC coupons (Hexoloy™, Carborundum, Niagara Falls, NY) or melt infiltrated

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(MI) SiC/SiC (Honeywell Composites, Phoenix, AZ). Two types of silicon bond coat were used: silicon surface layer on as-processed MI or plasma-sprayed silicon.

To determine chemical/environmental durability, EBC-coated MI or SiC coupons were thermally cycled in a water vapor furnace (3). For silica volatilization studies, both high-pressure burner rig (HPBR) tests (2) of EBC-coated MI and thermogravimetric analysis (TGA) studies of hot pressed EBC coupons in water vapor were used. Typically, the thermal cycling tests in water vapor were run at 1300 and 1400°C in 90% H₂O-balance O₂ at 1 atm (simulated lean combustion environments) using an automated thermal cycling furnace. The HPBR tests were run at 1300°C, 6 atm (pH₂O ~ 0.6 atm), fuel to air ratio = 0.065, and gas velocity ~ 24m / sec. Water vapor thermogravimetric analysis was conducted at 1200, 1300, 1400 and 1500°C in 50% H₂O-balance O₂ at 1 atm (simulated lean combustion environments). Tested samples were mounted in epoxy, polished to 1 μm using diamond suspension, and examined using scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), and electron microprobe analysis (EMPA).

3 Results and Discussion

3.1 Chemical / Environmental Durability

3.1.1 BSAS EBC

BSAS was identified as a promising EBC candidate because of its close CTE match with Si-based ceramics ($4\sim 5 \times 10^{-6}/^{\circ}\text{C}$) and low silica activity (< 0.1) (5). It also possesses excellent resistance to cracking in thermal cycling, presumably due to the low elastic modulus. Figure 1 shows a cross section of BSAS-coated MI after 100h at 1300°C with 2h furnace cycles in 90% H₂O. A thick (10 ~ 20 μm) reaction zone and large pores developed at the BSAS/silica interface. Analysis by EDS revealed that the reaction zone contained a high level of Si and a significant amount of Al and Ba (Sr peak overlapped with Si peak), suggesting a reaction between thermally-grown silica and BSAS. The reaction zone, which is amorphous according to Raman Spectroscopy (7), may be benign to coating durability as long as it remains solid. What is detrimental to the EBC durability is that the pores continue to grow and eventually coalesce, causing EBC delamination. Pores are attributed to the bubbling of gaseous species through the scale as the scale viscosity is significantly reduced due to contamination by oxides of Ba, Sr, and Al (9). Gaseous species include CO, CO₂, or Si(OH)₄, reaction products of oxidation of SiC. Therefore, the BSAS-silica chemical incompatibility at temperatures as low as 1200°C makes BSAS unsuitable as an EBC when applied directly on Si-based ceramics.

3.1.2 Mullite+BSAS/BSAS EBC

BSAS is still attractive as an EBC, as long as a suitable bond coat is available. Mullite, alone or modified by BSAS, showed adequate chemical compatibility with BSAS and excellent bonding to Si or Si-based ceramics. A mullite+BSAS/BSAS EBC exhibits excellent durability to 1000h at 1300°C, with limited BSAS-silica reaction and no pore formation (Fig. 2). The improved chemical compatibility of the mullite+BSAS/BSAS EBC compared with the BSAS EBC is due

to a small fraction of the EBC/substrate interface in contact with the BSAS. The BSAS-silica reaction is enhanced as the kinetics of silica formation and BSAS-silica reaction increase with temperature. At $T > 1400^{\circ}\text{C}$, the BSAS-silica reaction eventually produced a significant amount of low melting ($\sim 1300^{\circ}\text{C}$) $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-BaO-SrO}$ glasses, with subsequent spallation of EBC. The formation of low melting glasses is a key life-limiting factor for the mullite+BSAS/BSAS EBC system.

3.1.3 Mullite/BSAS EBC

A mullite/BSAS EBC can be as durable as mullite+BSAS/BSAS EBC at 1300°C as shown in Fig. 3a. A major disadvantage of the mullite bond coat compared with the mullite+BSAS bond coat is the difficulty in depositing crack-free mullite. There was a significant batch-to-batch variation in segmental cracks, implying a small margin of error in controlling the coating quality. Segmental cracks provide the path for water vapor and thus cause enhanced degradation (Fig. 3b), leading to reduced EBC life. Residual amorphous mullite and CTE mismatch are believed to be responsible for the segmental cracks (4). The fact that the deposition of residual amorphous mullite is sensitive to process variations indicates that residual amorphous mullite is key to the variation in segmental cracking. A major advantage of the mullite bond coat compared with the mullite+BSAS bond coat is the absence of low melting glass formation as BSAS-silica reaction is eliminated. In the absence of glass formation, however, BSAS suffers a different type of degradation at $T > 1400^{\circ}\text{C}$. Figures 4a and 4b show cross sections of mullite/BSAS EBC on SiC after 180h and 20h at 1400°C (20h thermal cycles) and 1500°C (isothermal), respectively, in air. The BSAS surface began to show degradation at 1400°C , forming a porous structure (Fig. 4a), which became very severe at 1500°C as the porous structure spread over the entire BSAS layer (Fig. 4b). The cause of the degradation is not fully understood. The formation of a porous structure is likely to be a key life-limiting factor at $T > 1400^{\circ}\text{C}$.

3.2. Silica Volatility

Figure 5 shows the plots of weight change versus time for uncoated and EBC-coated SiC at 1300°C in the HPBR (6 atm, $p_{\text{H}_2\text{O}} \sim 0.6$ atm, gas velocity $\sim 24\text{m/sec}$, fuel to air ratio = 0.065). Each datum in the plots represents one thermal cycle since the test was interrupted to measure the weight. The linear weight loss of uncoated CVD SiC and MI was due to the volatilization of silica by water vapor. Mullite+BSAS/BSAS- and mullite/BSAS-coated MI also showed a slight weight loss. Cross sections of mullite+BSAS/BSAS- and mullite/BSAS-coated MI showed excellent adherence and minimal oxidation, implying that the weight loss was mainly due to the volatilization of silica from BSAS.

Figure 6 shows the plots of weight change versus time for hot pressed monolithic BSAS exposed to 50% H_2O -balance O_2 at $1200\text{-}1500^{\circ}\text{C}$ in thermogravimetry (1atm, gas velocity = 4.4 cm/sec). Linear weight loss was observed at all temperatures with the rate increasing with temperature. The weight loss rate at 1300°C was converted to the weight loss rate at the HPBR condition (6 atm, $p_{\text{H}_2\text{O}} = 0.6$ atm, $V_g = 24\text{m/sec}$) using the following silica volatility equation, which assumes Si(OH)_4 as the sole reaction product (2),

$$\text{Volatility} \propto V_g^{0.5} (p_{\text{H}_2\text{O}})^2 / P_{\text{tot}}^{0.5} \quad (1)$$

where V_g is the gas velocity, p_{H_2O} is the water vapor pressure, and P_{tot} is the total pressure. The converted rate from the thermogravimetry measurements (3.3×10^{-3} mg/cm²-h) agreed fairly well with the rate determined using the HPBR ($\sim 6 \times 10^{-3}$ mg/cm²-h). Projected recession of BSAS, after 1000h at 6 atm, $p_{H_2O} = 0.6$ atm, and $V_g \sim 24$ m/sec, from equation (1) and the silica volatility data from thermogravimetry was 4, 18, and 72 μ m, at 1300, 1400, and 1500°C, respectively. The recession will be even higher in typical engines that run at higher pressure and gas velocity. Based on BSAS thickness of ~ 250 μ m (~ 10 mil), typical of current YSZ TBCs in aero gas turbines, the volatility of BSAS will be another key life-limiting factor for over several thousand hours of operation at $T > 1400^\circ\text{C}$.

5. Conclusions

Chemical/environmental durability and silica volatility all suggest that the upper temperature limit of EBCs based on mullite and BSAS, for several thousand hours of life, is $\sim 1400^\circ\text{C}$. Since the temperature drop through the EBC will lower the temperature at the EBC/CMC interface below 1400°C , the BSAS-silica reaction is not likely to be as critical as BSAS degradation by the formation of a porous structure and silica volatilization at $\sim 1400^\circ\text{C}$. The characterization of EBCs under realistic temperature gradients in steam environments is needed to provide more accurate life projections. The further development of EBCs, with higher temperature capability and lower thermal conductivity than today's EBCs, is necessary to realize the full potential of Si-based ceramics in gas turbine engines.

Acknowledgements

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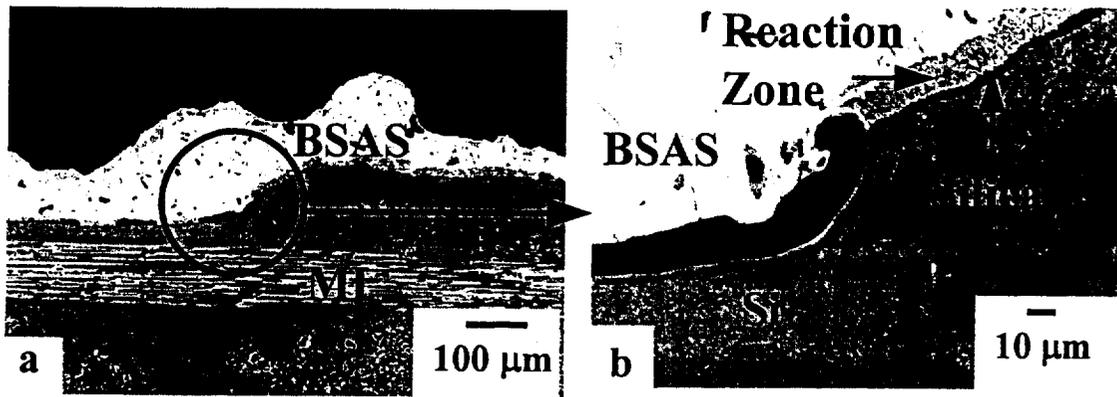


Fig. 1 Cross section of BSAS-coated MI after 100h in 90% H₂O -balance O₂ at 1300°C with 2h furnace cycles

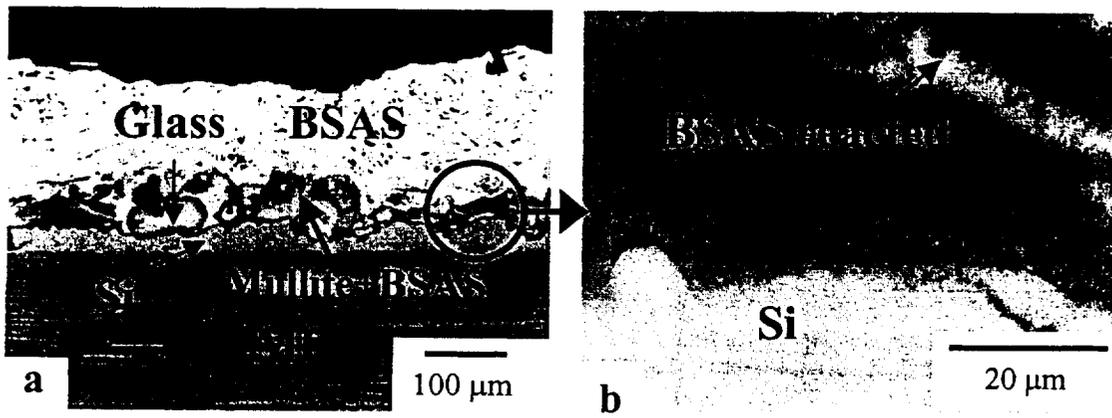


Fig. 2 Cross section of mullite+BSAS/BSAS on MI after 1000h in 90% H₂O -balance O₂ at 1300°C with 1h furnace cycles

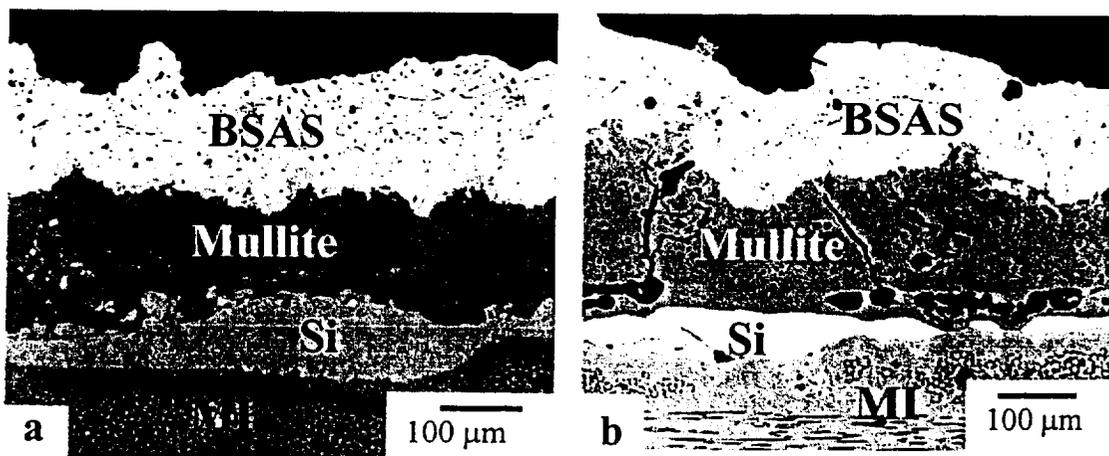


Fig. 3 Cross sections of mullite/BSAS on MI after 1000h in 90% H₂O -balance O₂ at 1300°C with 1h furnace cycles (a and b are from two different batches of coatings)

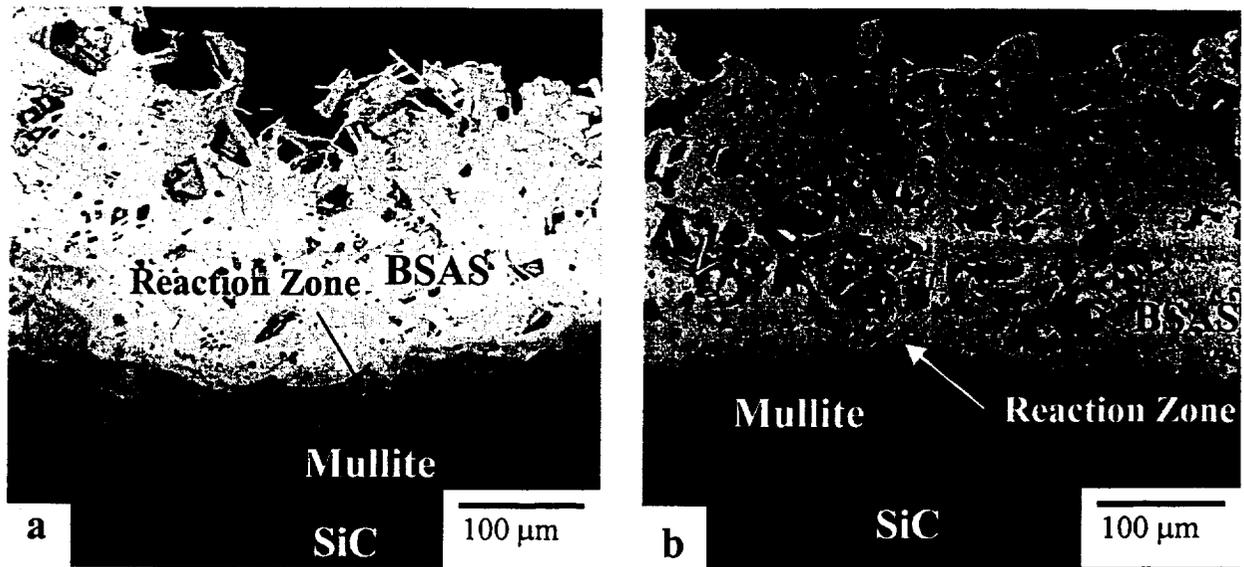


Fig. 4 Cross section of mullite/BSAS on SiC after thermal exposures in air. The reaction zone is a diffusion zone between mullite and BSAS.
 a: 180h, 1400°C-20h furnace cycles; b: 20h, 1500°C isothermal furnace

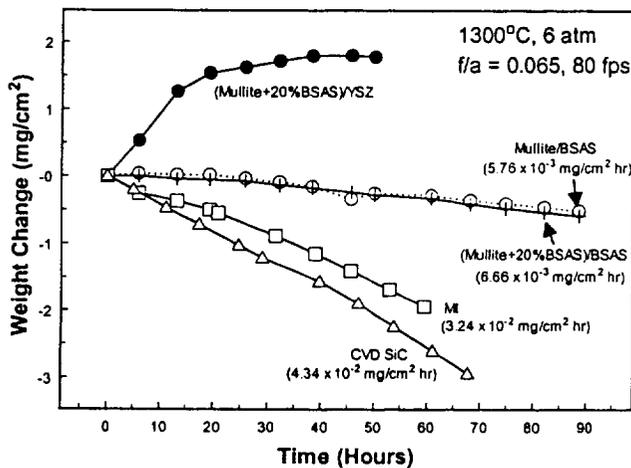


Fig. 5 The plots of weight change vs. time for uncoated and EBC-coated SiC in high pressure burner rig (1300°C, 6 atm, $p_{H_2O} \sim 0.6$ atm, gas velocity ~ 24 m/sec, fuel to air ratio = 0.065)

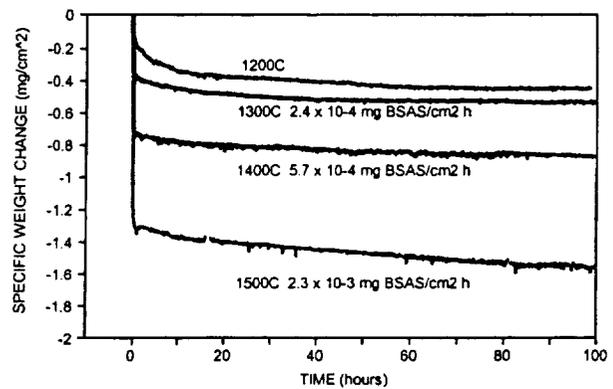


Fig. 6 The plots of weight change vs. time for hot pressed BSAS in TGA (1200°C-1500°C, 1atm, $p_{H_2O} = 0.5$ atm, gas velocity = 4.4 cm/sec)